SYNOPSIS

"Development of multiferroic Thin Films and its Study for non-volatile memory device Application"

Submitting to

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Title

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1. Introduction:

The concept of altering resistance of metal oxide thin film under external electrical stress opened a new remarkable research area attractive for next-generation non-volatile memories with scenario including very high-density integration and multi-state logic implementation [1-4]. Among the non-volatile memories considered till now, the resistive random access memory (RRAM), employ reversible resistive switching (RS) behaviour, is increasingly important due to its simple structure, long retention time, small size, and fast switching speed[5-6]. Simplicity of the geometrical structures (metal/meal oxide/metal) makes the resistance switching extremely attractive and promising.

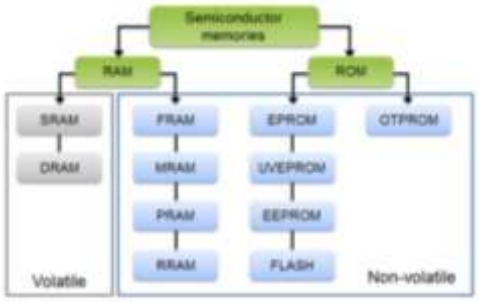

Figure 1. Categories of standard semiconductor memories and emerging memories, e.g. FRAM, MRAM, PRAM and RRAM.

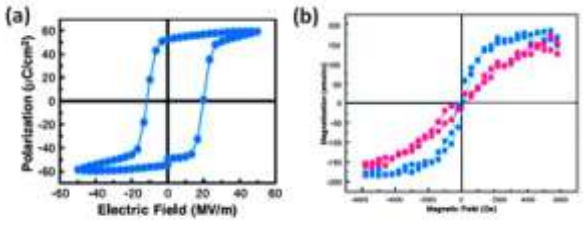

Figure 2: (a) Ferroelectric and (b) Ferromagnetic behaviour of $BiFeO_3$ thin film

Many transition metal oxide (TMO) materials possess the RS behaviour and among them perovskite materials also show excellent RS[5,7]. Recently, this phenomenon has also been found in $BiFeO_3$ (BFO) films[8-10]. Usually BFO is an extensively studied multiferroic material, which exhibit ferroelectric and ferromagnetic behaviours (Figure 2) simultaneously[11]. As to this, BFO has been widely studied since it exhibits a high Curie temperature (Tc ≈ 1100 K), a high N´eel temperature (T_N ≈ 643 K) and a large remnant polarization over 90 μC/cm^2. Beside this, photo response is also one of the most viable properties of BFO and gain significance from last few years[8,12]. Numerous reports show photo-resistance and photo-voltaic effect in BFO hetrostrucutres and correlated it with band gap (~ 2.2 eV) of BFO[8], that is within visible light range, may be due to the energy band bending at domain walls[13]. The output photo-response, which may be a photo-current or photo-voltage, is a function of the product of the remnant polarization from a previously applied polarization voltage and the incident light intensity[14-15]. Owing to its remarkable properties it attracted much attention for multifunctional applications.

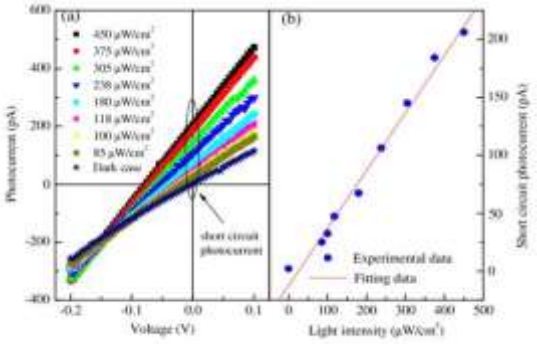

Figure 3: Photoresponse of $BiFeO_3$ thin film

Resistive switching (RS) implies a sudden change in electrical characteristics of oxide material under applied voltage, namely a highly resistive state (HRS) and low resistance state (LRS). Several driving mechanisms have been proposed to explain this, e.g. generation and rupture of conductive filament, Schottky barrier and space charge trap and detrap in thin films. These mechanisms can be categorized into the bulk-limited and interface-limited conduction modulations. Bulk-limited mechanisms originate from the formation and rupture of conductive tracks 'filaments' in an insulating film and interface-limited takes place at the interface between different oxides or between the metal-electrode and the oxide.

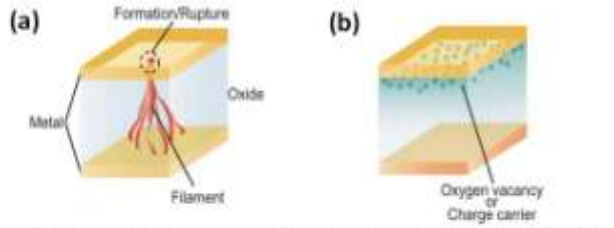

Figure 4: (a) Filamentary and (b) interface mechanism of resistive switching

Despite the RS mechanisms are diverse; all these mechanisms are partially or mostly related to the movement and sequential redistribution of oxygen vacancies along film. When oxygen vacancies act as donor impurities, an increase in local oxygen vacancy concentration by external stimulus (e.g. electric fields) can make it highly conductive n-type semiconductor.

2. Review of Literature and Development in the Subject:

Till today, various metal oxides have reported reversible RS behaviour. These oxides are generally called as wide band gap semiconductors mainly due to their bandgaps which are larger than those of conventional semiconductors. Moreover, the electrical characteristics of these oxides are tuneable through impurity doping. The tuneable electrical characteristics of these oxides are critical to elucidate the RS behaviour.

The most popular way to control the electric properties of oxides is via doping which changes the oxygen stoichiometry of the film. In many oxides interesting phenomenon like luminescence, high temperature superconductivity, magneto-resistance arise due to doping. Proper doping changes the electronic conductivity of oxides by generating extra mobile charge carriers or oxygen vacancies. For this Co and Ca will be used as a dopant because it is well known that Co and Ca doping creates oxygen vacancies in oxides, especially complex oxide like BFO.

BFO receive a great importance since it show interesting electrical and optical characteristics. These properties can be potentially utilized for optoelectronics and memory device applications. BFO is widely studied multiferroic with high Curie temperature and high Neel temperature. A large remnant polarization over 90 $\mu C/cm^2$ is realized by a large displacement of the Bi-ions relative to the FeO_6 octahedra.

This work propose to investigated RS in undoped and doped polycrystalline BFO thin films fabricated by a sol-gel assisted spin coating method. For this efficient and sensitive characterization techniques are going to be used to understand crystallinity, electronic structure, topography, molecular finger print, morphology and purity of the synthesized sample.

3. Objectives of Research/Proposed Hypothesis:

This work identify the fundamental physical mechanisms behind RS of intrinsic resistance (or state) of BFO thin film under various stimuli such as electrical field and dopant to yield enhanced functional properties. Particular emphasis is placed on control of the under pinning solid-state microstructure phenomenon that facilitates the modulation of electronic transport properties under external bias and dopant.

To achieve the above over all goals the proposal is made of specific aims

- To synthesize undoped and doped BFO thin films using a facile sol-gel assisted spin coating technique
- To understand structural, ferroelectric, optical, magnetic, electrical and electronic structure of the BFO thin film
- To probe the electronic structure of dopant and understanding the role of its intrinsic properties on charge transport.
- To investigate RS characteristics of the BFO thin film
- Use the understandings from above to propose a model based on switching action, electronic structure of dopant and dopant-defect interaction.

4. Methodology to be adopted:

The central theme founding this work is the fabrication and engineering of doped metal oxide materials for enhancement in resistive switching. This work is designed to run on three stages for three years.

Stage 1: Fabrication of thin films of undoped and (Co and Ca) doped BFO:

The primary motivation behind this stage is to investigate the growth and physical properties of polycrystalline BFO films with doping elements. Individual goals of this stage is

a. Fabrication of high quality doped BFO thin films on metal substrate via sol-gel assisted spin coating at SRTMUN and their characterization using XRD, TGA, SEM and AFM.
b. Initial investigation of resistive switching in these films with respect to their thickness and dopant concentration at SRTMUN.

Stage 2: Establish the electronic structure of the films and correlate with its switching properties:

a. Investigation of the electronic structure of the high quality doped BFO thin films using X-ray photoelectron spectroscopy (XPS) at NCL, Pune.
b. Correlating the role of deposition parameters, dopant and its concentration with the observed resistive switching.

Stage 3: Investigation of intrinsic nature of dopant:

The dopants used in this work are magnetic elements. Even if they are doped at atomic levels, they eventually induce dilute magnetism. Therefore it is interesting to investigate the magnetic properties of these doped films.

a. Investigation of optical properties of doped BFO films at various concentrations of Co and Ca.
b. Use of the above investigated properties of the dopant for determination of viable switching material based on doped BFO film.

During the final stage of the work, efforts will be made to fabricate and demonstrate metal doped oxide as a functional material with improved switching characteristics for its viable application in current semiconductor market.

5. Importance of study/ Society application:

National status:
A number of important research outcomes addressing a variety of issues in this field have been supported and are in progress in various National laboratories and universities in the country funded by Government of India. Although it is difficult to summarize the whole effort, a representative cross section of ideas and strategies can be provided as follows: Dr. Satishchandra B. Ogale (resistive switching in epitaxial bismuth ferrite hetero-structures), Dr. K. Mukherjee (MIM capactir using porous alumina), Prof. A.K. Sood (resistive switching in ultrathin films of graphene and carbon nanotubes), Dr. B. R. Mehta (resistive switching in CuInO2–CuO bilayer structure), Prof. Pankaj Misra (ZnO based transparent resistive random access memory devices), Dr. P Bhattacharyya (Au/TiO2/Ti memory device), Dr. D. Kuberkar, etc.

International status:
Continuous advancement in integrated circuit technologies over the past decades have given us computers with powerful processing capabilities due to high-speed/high density memories and processors. Additionally, portable mobile electronic devices are heavily reliant on the development of high-density, high-speed and low-power memories. ‘Technological advanced materials plays frontier role at the present time and would continue to be so for several decades to come, if not more. It encompasses and addresses a wide variety of fields rated to devices, electronics, memories, etc.

In the specific research area to be focused upon in the proposed project, the international research is just beginning to grow creating a fairly open opportunities

for Indian science to take a lead and make a substantial impact. These developments are occurring in the domains of new device concept such as non-volatile memory. Few impressive examples who flourish the focus of this project are: Prof. R. Ramesh[17-19], Prof. Q. X. Jia[20], Prof. T. Wu[16], Prof. A. Sawa[5], etc. Lots of literature is available on various reputed research journals like: Nature, Science, Advanced Materials, Nano Letters, Advanced Functional Materials, etc.

Significance of the study

Scientifically the research output from this work will provide understanding to number of basic physical questions related to resistive switching in oxide thin films. This will investigate advanced functionalities of doped BFO material. This material is critical to the emerging field of oxide nano-electronics technology. In the last 3 years lots of papers have appeared in three of the highest cited journals for materials science-Nature, Science and Nature Materials. This is a strong indication of the intense interest in oxide thin films.

6. Proposed work Plan/ Formulation and Structure of Study: Year-wise Plan of work and targets to be achieved

First Year:

a. Initiate sol-gel synthesis of undoped BFO employing the available facilities.
b. Initiate and optimize solution based thin film growth methods (dip or spin coating) for functional oxide coatings.
c. Study effect of temperature on film morphology.
d. Establish and implement characterization strategies for the films and the nano-film hybrids.
e. Initiate testing of resistive switching properties of undoped BFO films.

Second Year:

a. Initiate and optimize sol-gel technique for doping of functional oxide with metal dopant.
b. Initiate and optimize thin film growth methods (dip or spin coating) for doped functional oxide coatings on various substrates.
c. Study effect of temperature and doping concentration on film morphology.
d. Perform extensive in-house characterizations including AFM, XRD, TGA, etc. as well as those involving external collaborations SEM-EDS, TEM and XPS.
e. Test of resistive switching properties of doped BFO films.

Third Year:

a. Review the status of progress during the first two years and to take appropriate steps towards the most effective utilization of the knowledge, facilities and experience during the remaining duration.
b. Continue to analyze the data obtained and proceed with publications/patenting as appropriate.
c. Prepare thesis for submission.

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